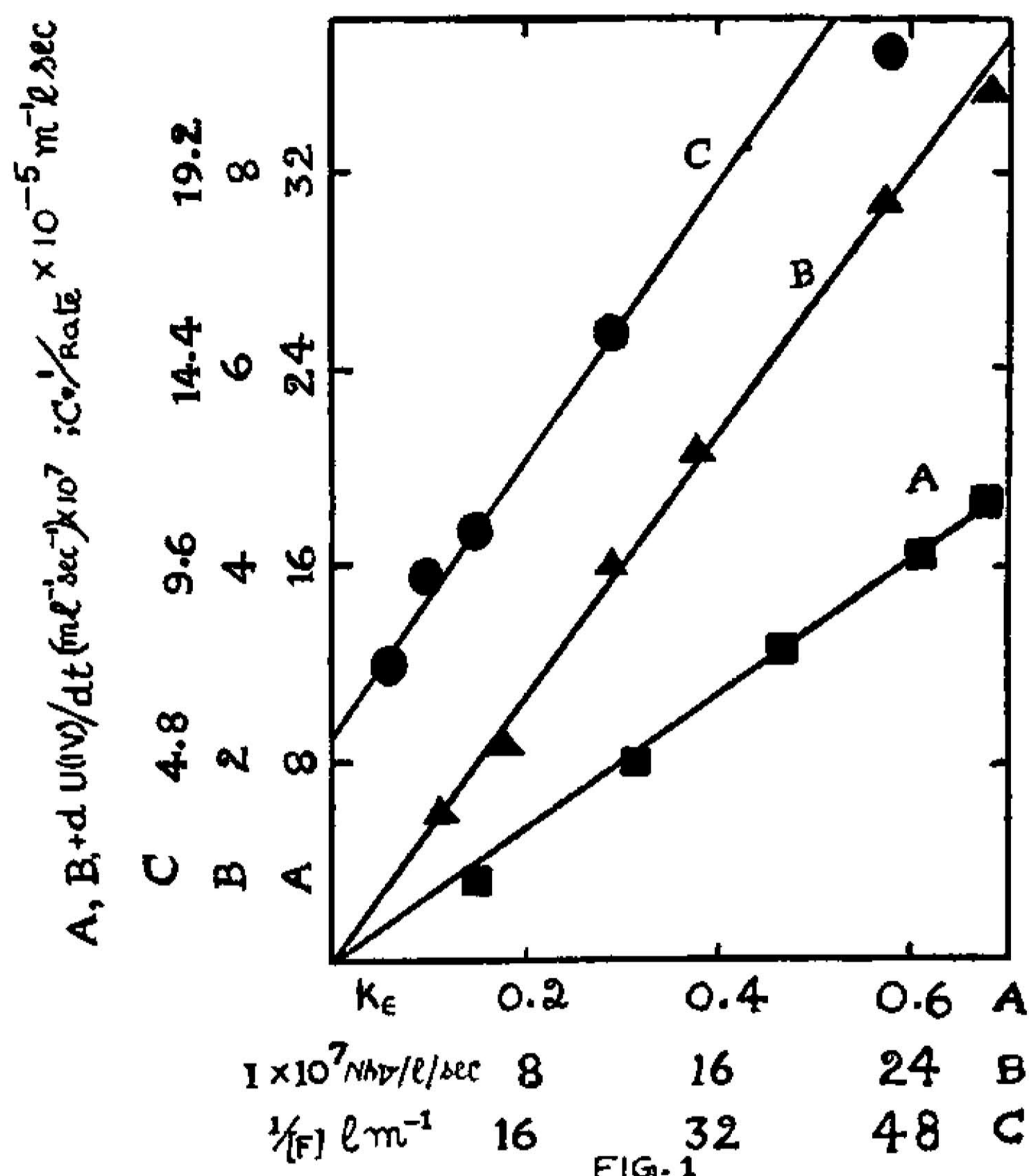


PHOTOCHEMICAL OXIDATION OF FORMALDEHYDE BY URANYL IONS [U(VI)] IN AQUEOUS SOLUTION

STUDIES reported so far on photochemical oxidation of organic substrates by uranyl ions in aqueous solution have been few; and even here conflicting opinions have been expressed with regard to nature of primary photochemical act in these reactions.¹⁻⁵ We have undertaken a systematic study of oxidation of aliphatic and aromatic aldehydes and we report briefly our results with formaldehyde as the substrate.

Oxidation of formaldehyde F (0.02 M to 0.2 M) by uranyl perchlorate (0.01 M to 0.05 M) in perchloric acid medium by light of $\lambda = 4350 \text{ \AA}$ (from a BTH 250-Watt high pressure mercury vapour lamp) under conditions of constant temperature ($35^\circ \pm 0.01^\circ \text{ C.}$), ionic strength ($\mu = 0.5$) and pH (< 2) has been carried out. A specially designed cell with stopper containing the reaction system has been used both for irradiation purposes as well as for subsequent absorbancy measurements at $670 \text{ m}\mu$ [for U(IV) production] in the Hilger-Watts H-700 Uvispek spectrophotometer. Formaldehyde in the system has been estimated from absorbancy at $585 \text{ m}\mu$ of formaldehyde-chromotropic acid complex. Potassium ferrioxalate as well as uranyl oxalate actinometers have been used for determination of light intensities (I). The rate measurements [relating to U(IV) production] against variations in (a) light absorption fraction (k_e) by U(VI),

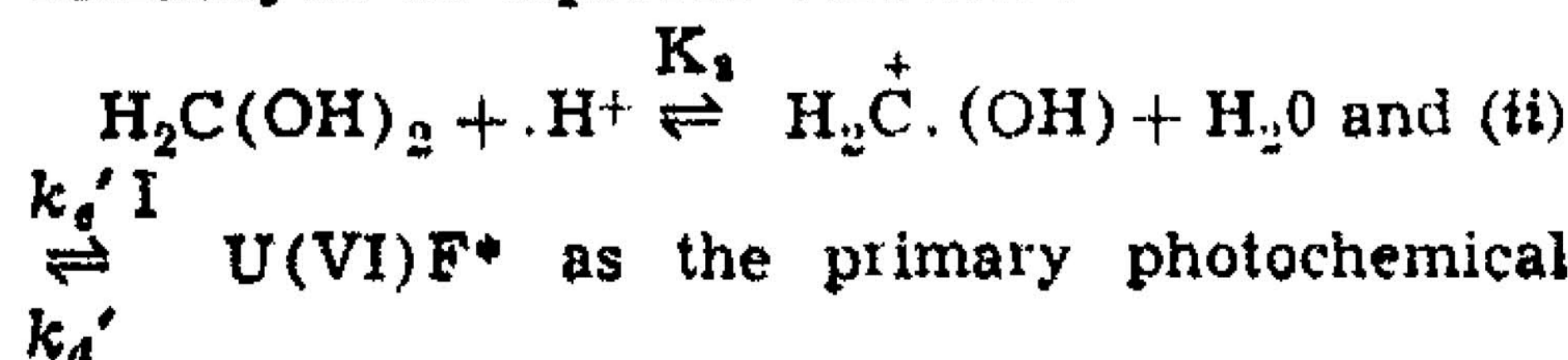
(b) formaldehyde concentration (F), (c) hydrogen-ion concentration (H^+) have been followed and a rate equation established. Effects of temperature as well as ionic strength on rate have also been studied. We report briefly our results: (i) The dark reaction between $\text{U(VI)} + \text{F}$ ($35^\circ\text{--}80^\circ \text{ C.}$) is totally absent; (ii) undeaerated system on irradiation produces no U(IV); (iii) direct proportionality between (a) rate and light intensity (Fig. 1, B), (b) rate and k_e (Fig. 1, A); the net quantum yield for



U(IV) production remains constant at ~ 0.5 , (c) reciprocal rate and reciprocal (F) (Fig. 1, C), (d) inverse proportionality between rate and (H^+), (e) slight increase of rate with μ , and (f) independence of rate with temperature. Effect of initially added U(IV) or formic acid (both are products of the reaction) which merited a thorough study could not be investigated because the former acts as an inner filter and the latter forms a complex with U(VI) complicating the kinetic features of the reaction.

We conclude that most of the observed kinetic features may be explained on the basis

of (i) a transient equilibrium $\text{U(VI)} + \text{F} \xrightleftharpoons{K_1} \text{U(VI)} \dots \text{F}$ and the equilibrium for the formaldehyde in aqueous solution:



and dark back reactions. The subsequent dark reaction $U(VI)F^* \xrightarrow{k_1} U(V) + H^+ + F^\bullet$ ($F^\bullet =$ radical fragment from F) is the rate determining step while reactions between $U(VI) + F^\bullet$, disproportionation of $U(V)$ to $U(IV)$, etc., are all fast. Assuming stationary state kinetics for $[U(VI)F]^*$ and same extinction for $U(VI)$ and $U(VI)F$, it has been deduced that:

$$\text{Rate} = \frac{k_1'}{1 + K_1 F_e}$$

when

$$k_1' = \frac{2k_1 k_e I}{(k_d' + k_1)}$$

$F_e =$ equilibrium F

$k_e =$ light absorption fraction by
 $U(VI)$ and $U(VI) \cdots F$

and

$$\frac{1}{\text{Rate}} = \frac{1}{k_1'} + \frac{1 + K_2 (H^+)}{k_1' K_1 F_{\text{total}}}$$

From the plot of $1/\text{rate}$ vs. $1/F_{\text{total}}$, the values of constants evaluated as a first approximation are:

$$k_1 = 0.4367; \quad K_2 = 4.7 \text{ lm.}^{-1}$$

The postulate for formation of a transient photosensitive cluster is in accord with views of Heidt and Moon³ and of Weigert⁶ earlier. Total absence of dark reaction between $U(VI)$ and F and absence of any absorption at $435 \text{ m}\mu$ by F and proportionality between $1/\text{rate}$ and $1/F$ indicates that excitation of $U(VI)F$ is indeed the primary step. Absence of $U(IV)$ in the underaerated irradiated systems suggests oxidation of $U(V)$ to $U(VI)$ by oxygen.

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